

# PATENT ABSTRACTS OF JAPAN

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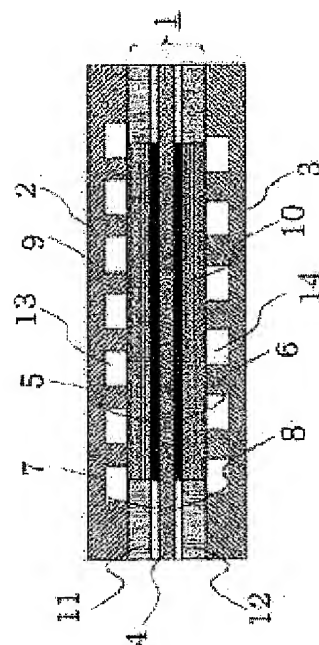
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## (54) FUEL CELL AND ITS MANUFACTURING METHOD

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a fuel cell equipped with a solid polymer electrolyte film supported by an electrode base material under uniform pressure without fear of damage of the film, in spite of stress if any due to repetition of drying and dampening, as well as its manufacturing method.

**SOLUTION:** The fuel cell, provided with a membrane electrode assembly made by pinching a negative electrode catalyst layer and a positive electrode catalyst layer pinching the center part of a solid polymer electrolyte film from both sides with a fuel electrode base material and an oxidant electrode base material with the same outer shape as the solid polymer electrolyte film from outside, is further provided with an outer edge part surrounding the negative electrode catalyst layer and the positive electrode catalyst layer out of the solid polymer electrolyte film, and a step-eliminating member between the fuel electrode base material and the oxidant electrode base material.



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## CLAIMS

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[Claim(s)]

[Claim 1]

In a fuel cell which has a membrane electrode zygote which pinches further a negative-electrode catalyst bed and a positive electrode catalyst layer which were joined to a center section of solid polyelectrolyte membrane from both sides from both sides with a fuel electrode substrate of a bigger area than the above-mentioned negative-electrode catalyst bed, and an oxidant electrode substrate of a bigger area than the above-mentioned positive electrode catalyst layer, A fuel cell, wherein a level difference dissolution member is provided in a crevice between outer edge sections, the above-mentioned fuel electrode substrates, and the above-mentioned oxidant electrode substrates which surround the above-mentioned negative-electrode catalyst bed and the above-mentioned positive electrode catalyst layer among the above-mentioned solid polyelectrolyte membrane, respectively.

[Claim 2]

The fuel cell according to claim 1, wherein the above-mentioned level difference dissolution member consists of thermoplastics.

[Claim 3]

The fuel cell according to claim 1, wherein the above-mentioned level difference dissolution member consists of a porous body with which thermoplastics was filled up.

[Claim 4]

A fuel electrode substrate with which the above-mentioned negative-electrode catalyst bed was provided in a center section so that a negative-electrode catalyst bed and a positive electrode catalyst layer might touch solid polyelectrolyte membrane, and an oxidant electrode substrate with which the above-mentioned positive electrode catalyst layer was provided in a center section are laminated to both sides of the above-mentioned solid polyelectrolyte membrane, A thermoplastic resin sheet of frame shape is laminated so that the above-mentioned negative-electrode catalyst bed may be surrounded in a field which has not met the above-mentioned solid polyelectrolyte membrane of the above-mentioned fuel electrode substrate, A thermoplastic resin sheet of frame shape is laminated and a layered product is formed so that the above-mentioned positive electrode catalyst layer may be surrounded on the other hand in a field which has not met the above-mentioned solid polyelectrolyte membrane of the above-mentioned oxidant electrode substrate,

A manufacturing method of a fuel cell having the process of carrying out application-of-pressure heating from both sides of the above-mentioned layered product, and manufacturing a membrane electrode zygote.

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[Translation done.]

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[Field of the Invention]

[0001]

This invention relates to a fuel cell generated using an electrochemical reaction, and a manufacturing method for the same.

[Background of the Invention]

[0002]

A fuel cell is a device which transforms chemical energy into electrical energy directly by intervening an electrolyte membrane, making one pair of electrodes counter, supplying fuel to the electrode of one of these, supplying an oxidizer to the electrode of another side, and making fuel and an oxidizer react electrochemically within a fuel cell. Among this fuel cell, since the polymer electrolyte fuel cell uses the solid polyelectrolyte membrane which has proton conductivity as an electrolyte membrane, the high-output characteristic is obtained.

Electrochemical reaction continues this polymer electrolyte fuel cell by continuing supplying reactant gas. The ion conductivity of an electrolyte membrane which plays an important role by electrochemical reaction at this time is proportional to the moisture content of solid polyelectrolyte membrane mostly. Since the moisture content of solid polyelectrolyte membrane is dependent on the humidity of reactant gas, reactant gas is humidified and it operates.

[0003]

However, since solid polyelectrolyte membrane will swell if it is shrunken and it absorbs moisture if it dries, stress starts solid polyelectrolyte membrane by repetition of operation and a stop.

When the air dry to the oxidizer feed hopper is supplied, solid polyelectrolyte membrane dries in the upstream region of an airstream way, and solid polyelectrolyte membrane carries out humidity with produced water in the downstream area. Thus, since stress was added to solid polyelectrolyte membrane, if solid polyelectrolyte membrane was not supported certainly, there was a possibility that solid polyelectrolyte membrane might be damaged.

Then, it processes to solid polyelectrolyte membrane and enables it to support solid polyelectrolyte membrane certainly in the conventional fuel cell. For example, solid polyelectrolyte membrane has a deenergization part which is not in contact with the energized part and one pair of electrodes which touch the electrode whose number area is larger than one pair of electrodes, and is one. The reinforcing member is contained in the boundary part of the energized part and deenergization part. The fluorine polymer is used as this reinforcing member's construction material (for example, refer to patent documents 1.).

However, stress concentrated on the boundary part of the energized part of solid polyelectrolyte membrane, and the deenergization part reinforced with the reinforcing member, and there was a possibility that a crack might arise along with a boundary part.

Then, the electrode substrate which supports solid polyelectrolyte membrane is reinforced, and it enables it to support solid polyelectrolyte membrane certainly. For example, it is elaborated by the eburnation agent which an electrode substrate is the same area as solid polyelectrolyte membrane, and the edge part of an electrode substrate becomes from adhesives. The gas seal of the solid polyelectrolyte membrane is supported and carried out in this elaborated edge part. The

dispersion of a polytetrafluoroethylene system is used as an eburnation agent, and it is elaborating by removing an after-impregnating solvent to the edge part (for example, refer to patent documents 2.).

As a reinforcement method of other electrode substrates, the thermosetting fluid compound in which injection molding is possible is impregnated and hardened to the sealing region which surrounds the power generation region of an electrode (for example, refer to patent documents 3.).

[0004]

[Patent documents 1] JP,2000-260443,A

[Patent documents 2] JP,H8-148170,A

[Patent documents 3] JP,2001-510932,A

[Description of the Invention]

[Problem(s) to be Solved by the Invention]

[0005]

However, in the reinforcement method of an above-mentioned electrode substrate, the thickness of the electrode substrate which contained the catalyst bed by the part, edge part, and power generation part of thickness of the catalyst bed formed in the electrode substrate differs. For this reason, the edge part of solid polyelectrolyte membrane differed in the pressure added to solid polyelectrolyte membrane via an electrode substrate from the exterior from the power generation part, and there was a problem that support in an edge part will become weak.

[0006]

The purpose of this invention is to provide the fuel cell which has solid polyelectrolyte membrane without fear of membrane failure, and its manufacturing method, even if it is supported with an electrode substrate also as that of a uniform pressure and the stress by desiccation and humid repetition is added.

[Means for Solving the Problem]

[0007]

In a fuel cell concerning this invention. In a fuel cell which has a membrane electrode zygote which pinches further a negative-electrode catalyst bed and a positive electrode catalyst layer which were joined to a center section of solid polyelectrolyte membrane from both sides from both sides with a fuel electrode substrate of a bigger area than the above-mentioned negative-electrode catalyst bed, and an oxidant electrode substrate of a bigger area than the above-mentioned positive electrode catalyst layer, A level difference dissolution member was provided in a crevice between outer edge sections, the above-mentioned fuel electrode substrates, and the above-mentioned oxidant electrode substrates which surround the above-mentioned negative-electrode catalyst bed and the above-mentioned positive electrode catalyst layer among the above-mentioned solid polyelectrolyte membrane, respectively.

[Effect of the Invention]

[0008]

Since the effect concerning the fuel cell of this invention cancels the level difference seen between the power generation part and outer edge section concerning a catalyst bed by a level difference dissolution member and supports an electrolyte membrane evenly by the catalyst bed and a level difference dissolution member, it can make uniform stress added to an electrolyte membrane. As a result, breakage of an electrolyte membrane can be prevented.

[Best Mode of Carrying Out the Invention]

[0009]

Embodiment 1.

Drawing 1 is a sectional view of the polymer electrolyte fuel cell concerning this embodiment of the invention 1.

The cell of this polymer electrolyte fuel cell (a fuel cell is called hereafter.) has the conductive oxidizer separator board 2 and the conductive fuel separator board 3 which pinch the membrane electrode zygote 1 and its membrane electrode zygote 1 from both sides.

This membrane electrode zygote 1 The solid polyelectrolyte membrane of proton conductivity. (An electrolyte membrane is called hereafter.) Each periphery of 4, the positive electrode

catalyst layer 5 which touches the center section of one side of the electrolyte membrane 4, the negative-electrode catalyst bed 6 which touches the center section of other one side of the electrolyte membrane 4, the positive electrode catalyst layer 5, and the negative-electrode catalyst bed 6 is touched, It has [ the level difference dissolution members 7 and 8, and the positive electrode catalyst layer 5 and the level difference dissolution member 7 which faced the outer edge section of the electrolyte membrane 4 ] the wrap fuel electrode substrate 10 for the wrap oxidant electrode substrate 9, and the negative-electrode catalyst bed 6 and the level difference dissolution member 8. The outer edge sections 11 and 12 which the level difference dissolution members 7 and 8 of the oxidant electrode substrate 9 and the fuel electrode substrate 10 face, respectively are filled up with thermoplastics.

[0010]

The oxidant gas passage 13 which pours an oxidizer is established in the field where the conductive oxidizer separator board 2 faces the oxidant electrode substrate 9. The fuel gas flow route 14 which pours fuel is formed in the field where the conductive fuel separator board 3 faces the fuel electrode substrate 10. This oxidant gas passage 13 extends in the outer edge section of the conductive oxidizer separator board 2, and stands in a row in the hole further drilled in the outer edge section of that conductive oxidizer separator board 2 by the thickness direction. When laminating two or more cells, this hole is connected with the hole established in the conductive fuel separator board 3 of the cell laminated up and down, and is connected with the hole further established in the conductive oxidizer separator board 2 on it. An oxidizer is supplied there by using as an oxidizer feed hopper the hole established in the conductive oxidizer separator board 2 of the cell laminated on the top. The oxidizer which remained from there by using as an oxidizer outlet the hole established in the conductive fuel separator board 3 of the cell laminated at the bottom on the other hand is discharged. Supply and discharge are made the same also about fuel.

[0011]

The electrolyte membrane 4 is the Nafion (registered trademark) film whose outside is a perfluoro sulfonic acid film whose thickness is 50 micrometers in 10 cm x 20 cm. An outside is laminated at 7 cm x 14 cm, and, as for the positive electrode catalyst layer 5, thickness is laminated for the mixture of the carbon black particle and perfluoro system polymer electrolyte in which platinum was supported 50% of the weight by one side of the center section of the electrolyte membrane 4 at 14 micrometers. 7 micrometers of positive electrode catalyst layers 5 are stuffed into the oxidant electrode substrate 9, and the level difference of the surface of the oxidant electrode substrate 9 and the field facing the electrolyte membrane 4 of the positive electrode catalyst layer 5 has become 7 micrometers.

An outside is laminated at 7 cm x 14 cm, and, as for the negative-electrode catalyst bed 6, thickness is laminated by the opposite side of the field in which the positive electrode catalyst layer 5 of the center section of the electrolyte membrane 4 was formed for the mixture of the carbon black particle and perfluoro system polymer electrolyte in which the platinum \*\*RUTENIUMU system alloy was supported 50% of the weight at 14 micrometers. 7 micrometers of negative-electrode catalyst beds 6 are stuffed into the fuel electrode substrate 10, and the level difference of the surface of the fuel electrode substrate 10 and the field facing the electrolyte membrane 4 of the negative-electrode catalyst bed 6 has become 7 micrometers. The level difference dissolution members 7 and 8 consist of thermoplastics, and 10 cm x 20 cm, and the inside dimension of an outer size are [ 7 cm x 14 cm, and thickness ] 7 micrometers.

[0012]

The oxidant electrode substrate 9 and the fuel electrode substrate 10 are carbon paper of 80% of voidage, and an outside is [ thickness ] 300 micrometers in 10 cm x 20 cm. The hole of each outer edge section 11 and 12 of the oxidant electrode substrate 9 and the fuel electrode substrate 10 is filled up with the same thermoplastics as the level difference dissolution members 7 and 8.

The conductive oxidizer separator board 2 and the conductive fuel separator board 3 are black lead boards which combined black lead with resin, and the oxidant gas passage 13 and the fuel gas flow route 14 are formed in the field (7 cm x 14 cm) of the center section of those one side,

respectively.

[0013]

As for thermoplastics, polyolefin system resin is used. If it is resin which there is glass transition temperature as thermoplastics beyond the maximum temperature when the fuel cell is working, and has softening temperature below to the heat-resistant temperature of the electrolyte membrane 4, it is applicable to this invention. For example, there is copolymerization resin, such as polyolefin system resin and polyolefine which are represented by polyethylene and polypropylene, and polyvinyl acetate. The copolyamide system resin represented by Nylon 11, Nylon 12, etc. and the polyester system resin represented by polyethylene terephthalate and its copolymer are mentioned. Polybutylene resin, poly-methyl-methacrylate system resin, amorphous polyamide resin, etc. can be used.

[0014]

Next, the manufacturing method of this fuel cell is explained with reference to drawing 2. First, the oxidant electrode substrate 9 and the fuel electrode substrate 10 are cut down to 10 cm x 20 cm from the carbon paper (TGP-H-90 by Toray Industries, Inc.) of 300 micrometers in thickness, and 80% of voidage. The resin films 15 and 16 are cut down from the thermoplastics film of the polyolefin system of 300 micrometers of thickness to the shape of with the outer size of 10 cm x 20 cm, and an inside dimension of 7 cm x 14 cm RO. The flow beginning temperature of the thermoplastics of these resin films 15 and 16 is 130 \*\*. Flow beginning temperature was measured by the heating rate of 3 \*\* / min using the quantity-sized type flow tester (0.5 mm phix1 mmx10 kg/cm<sup>2</sup>). The electrolyte membrane 1 is started in 10 cm x 20 cm of outsides from the 50-micrometer-thick E. I. du Pont de Nemours Nafion film.

[0015]

Next, formation of the positive electrode catalyst layer 5 and the negative-electrode catalyst bed 6 is explained. As an anode catalyst, what supported platinum 50% of the weight on carbon black is used. Water 1 weight section and perfluoro system polyelectrolyte solution (FUREMION (registered trademark) 9% by Asahi Glass Co., Ltd. solution) 3 weight section are added to this anode catalyst 1 weight section, stirring mixing is carried out, and uniform anode catalyst paste is produced. As a negative-electrode catalyst, what supported the platinum \*\*RUTENIUMU system alloy 50% of the weight on carbon black is used. Water 1 weight section and perfluoro system polyelectrolyte solution (FUREMION (registered trademark) 9% by Asahi Glass Co., Ltd. solution) 6 weight section are added to this negative-electrode catalyst 1 weight section, stirring mixing is carried out, and uniform negative-electrode catalyst paste is produced. Next, it screen-stenciled and reduced pressure drying of this anode catalyst paste was carried out so that it might become 7 cm x 14 cm of outsides in the center section of the oxidant electrode substrate 9, and the positive electrode catalyst layer 5 was formed so that it might become 14 micrometers of after-desiccation thickness. It screen-stenciled and reduced pressure drying of the negative-electrode catalyst paste was carried out so that it might become 7 cm x 14 cm of outsides in the center section of the fuel electrode substrate 10, and the negative-electrode catalyst bed 6 was formed so that it might become 14 micrometers of after-desiccation thickness.

[0016]

Next, the member of a fuel cell is set to the plate 18 of the hotpress machine 19 like drawing 2. That is, the resin film 16 is set on the plate 18, and it puts in order of the oxidant electrode substrate 9 and the resin film 15 so that the fuel electrode substrate 10, the electrolyte membrane 4, and the positive electrode catalyst layer 5 may become downward, as the negative-electrode catalyst bed 6 is suitable up on it.

Next, these are put at a pressure 1 kg/cm<sup>2</sup> grade and the temperature of 150 \*\* with the plates 17 and 18, and it is made a vacua after that, and bolting pressure is increased to 5 kg/cm<sup>2</sup> and held for 3 minutes. The resin films 15 and 16 flow at this time, and the hole of the oxidant electrode substrate 9 and the fuel electrode substrate 10 is impregnated with that resin. The thermoplastics of the resin films 15 and 16 flows into the crevice between the electrolyte membrane 4 and the oxidant electrode substrate 9, and the crevice between the electrolyte



membrane 4 and the fuel electrode substrate 10. Next, bolting pressure was increased to  $10\text{kg}/\text{cm}^2$ , and was held for 2 minutes. Since the 14 positive electrode catalyst layers 5 and the negative-electrode catalyst bed 6 sank into the oxidant electrode substrate 9 and the fuel electrode substrate 10 selectively, respectively and became a thickness of 7 micrometers at this time, temperature was dropped to the room temperature. While the hole of the outer edge sections 11 and 12 of the oxidant electrode substrate 9 and the fuel electrode substrate 10 is fulfilled by thermoplastics, the crevice between the oxidant electrode substrate 9 and the fuel electrode substrate 10, and the electrolyte membrane 4 is buried, and the level difference dissolution members 7 and 8 are formed. Although resin was flowing into the portions of the oxidant electrode substrate 9 with which the positive electrode catalyst layer 5 and the negative-electrode catalyst bed 6 touched, and the fuel electrode substrate 10 by a width of about 0.5 mm, the losses of the usable area of an electrode were about 2% and a grade which can be disregarded. Excessive resin was disturbing from the heel of the oxidant electrode substrate 9 and the fuel electrode substrate 10. Thus, the cell of the fuel cell shown in drawing 1 was able to be formed.

[0017]

Although the inside dimension of the hole of the center of the resin films 15 and 16 was made into the same shape as the outside of the positive electrode catalyst layer 5 and the negative-electrode catalyst bed 6 in this Embodiment 1, most losses of the active electrode area were able to be abolished by enlarging the inside dimension of a central hole 1 mm.

[0018]

Next, operation of a fuel cell is explained. Oxygen as an oxidizer supplied from the oxidizer feed hopper which the conductive oxidizer separator board 2 does not illustrate passes along the oxidant gas passage 13, diffuses the inside of the oxidant electrode substrate 9, and is supplied to the positive electrode catalyst layer 5. On the other hand, like air, hydrogen as fuel passes along the fuel gas flow route 14, diffuses the inside of the fuel electrode substrate 10, and is supplied to the negative-electrode catalyst bed 6. Since the positive electrode catalyst layer 5 and the negative-electrode catalyst bed 6 are electrically externally connected at this time, in the positive electrode catalyst layer 5, the reaction of a formula (1) arises and it is discharged from the oxidizer outlet which unreacted oxygen and water do not illustrate through the oxidant gas passage 13. At this time, by the negative-electrode catalyst bed 6, the reaction of a formula (2) arises and unreacted hydrogen is discharged from the fuel outlet which is not similarly illustrated through the fuel gas flow route 14.

Anode reaction:  $2\text{H}^+ + 2\text{e}^- + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$  (1)

Negative-electrode reaction:  $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$  (2)

At this time, hydrogen is ionized on the negative-electrode catalyst bed 6, and it becomes a proton, moves on the positive electrode catalyst layer 5 with water in the inside of the electrolyte membrane 4, it reacts to oxygen, and water is produced.

[0019]

Next, in order to do the fuel cell and comparative study of this embodiment of the invention 1, the fuel cell of the comparative example shown in drawing 3 was produced. The places where the fuel cell of this comparative example differs from the fuel cell of Embodiment 1 are the oxidant electrode substrate 20, the fuel electrode substrate 21, and the gasket 22. Since others are the same, explanation of the same portion is omitted.

In drawing 3, the construction material and thickness of the oxidant electrode substrate 20 and the fuel electrode substrate 21 are the same as that of Embodiment 1. The outside dimension of the oxidant electrode substrate 20 and the fuel electrode substrate 21 is the same as the outside dimension of the positive electrode catalyst layer 5 and the negative-electrode catalyst bed 6. Again. The positive electrode catalyst layer 5 and the negative-electrode catalyst bed 6 also give a hotpress beforehand, and have embedded it only 7 micrometers at the oxidant electrode substrate 20 and the fuel electrode substrate 21. The gasket 22 was pierced and prepared for the with the outside of 10 cm x 20 cm, and an inside dimension of 8 cm x 15 cm

hollow square shape from the polyolefin-system-resin board. These were laminated like drawing 3 and the cell of the fuel cell of a comparative example was produced.

[0020]

The short stack was made as an experiment using four cells of this fuel cell, and operation evaluation was carried out. The fuel cell of the comparative example also contrasted by carrying out operation evaluation in parallel using four cells.

Where the temperature of these short stacks is kept at 80 \*\*, air of 65 \*\* of dew point was carried out, and generating operation was carried out with an about 50% of capacity factor flow sink, and the current of 25A. The refining imitation gas (75% of hydrogen, the remaining carbon dioxide) which contains 20 ppm of carbon monoxide as fuel at this time was supplied with 80% of the fuel utilization rate. At this time, the relative humidity of an oxidizer feed hopper will be 53%. On the other hand, in the oxidizer outlet, in order that water might generate by a fuel cell reaction, the moisture content in the air increased and relative humidity reached to 80%.

Therefore, in the field which corresponds upstream of air, the electrolyte membrane 4 dries and ion resistance increases. On the other hand, the moisture content of the electrolyte membrane 4 increases with produced water, and ion resistance decreases in a downstream area. At this time, the voltage of the cell of an early fuel cell was set to 750 mV, and open-circuit voltage was also set to 960 mV. And the cycle of having operated for 8 hours and stopping for 8 hours (load and a gas stop, a temperature room temperature) was repeated. The voltage and open-circuit voltage of a cell for every operation time are shown in drawing 4. AL in drawing 4 is the average cell voltage at the time of 25A load of the fuel cell of Embodiment 1, and AO is open-circuit voltage. On the other hand, BL and BO are the average cell voltage and open-circuit voltage at the time of 25A load of the fuel cell of a comparative example.

[0021]

Although the fall of the characteristic is seen with progress of operation time in the fuel cell of Embodiment 1, Even if 1000 hour had passed, the cell voltage at the time of 25A load stopped at falling only by 10 mV from the cell voltage 740 mV and in early stages of an examination, and open-circuit voltage also fell only several millivolts from the value 955 mV and in early stages of an examination. On the other hand, although the fuel cell of the comparative example showed the characteristic same till 600 hours as the fuel cell of Embodiment 1, the open-circuit voltage of one copy fell to 700 mV or less suddenly after it. Since control of the temperature of a cell became impossible, when operation was stopped and it decomposed, the electrolyte membrane 4 of the gasket 22 of the cell with which open-circuit voltage fell, and the gap part of an electrode substrate was torn. Although the electrolyte membrane 4 did not carry out the tear, wrinkles had occurred in the electrolyte membrane 4 of the gap part of the gasket 22 and the electrode substrates 20 and 21, and other cells were weak. The combination of an operating temperature and humidity was changed and this examination was tried 5 times. The outline of the test result is shown in drawing 5. In the fuel cell of Embodiment 1, the difference showed the characteristic where what existed was stabilized at the amount of characteristics degradation, and the examination has been continued. On the other hand, although the case 2 where humidification temperature was high showed the stability of the same characteristic as the fuel cell of Embodiment 1 in the fuel cell of the comparative example, on the conditions that humidification temperature is low, open-circuit voltage fell in hundreds of hours, and the electrolyte membrane 4 was damaged.

[0022]

In the fuel cell of this Embodiment 1, since the electrolyte membrane of the outer edge section was insulated electrically, even if the electrolyte membrane 4 was touching with the open air, the ion conduction course from an internal fuel passage became extremely long, and did not form a partial cell substantially, and worries about corrosion or a fuel loss disappeared.

[0023]

Since such a fuel cell cancels the level difference seen by the level difference dissolution members 7 and 8 between the power generation part and outer edge section concerning the catalyst beds 5 and 6 and supports the electrolyte membrane 4 evenly by the catalyst beds 5 and 6 and the level difference dissolution members 7 and 8, it can make uniform stress added to



the electrolyte membrane 4. As a result, breakage of an electrolyte membrane can be prevented.

[0024]

Since thermoplastics flows into the crevice between the electrolyte membrane 4 and the electrode substrates 9 and 10 at the time of a hotpress, the manufacturing method of such a fuel cell, The field which absorbs dispersion in the size of the member used for a fuel cell, etc., and touches the electrolyte membrane 4 of the catalyst beds 5 and 6 and the level difference dissolution members 7 and 8 can be made flat.

[0025]

If thermoplastics is used, it will become the resin layer in which the resin which constitutes the level difference dissolution members 7 and 8, and the resin impregnated with the hole of the electrode substrates 9 and 10 continued, and gas-seal nature will improve.

[0026]

The flow starting point is a 110 \*\* (melting point of 92 \*\*) thing about the thermoplastics used for the level difference dissolution member, and the membrane electrode zygote 1 was produced, and after laminating the membrane electrode zygote 1, the conductive oxidizer separator board 2, and the conductive fuel separator board 3 one by one and forming a cell, it heated at 110 \*\*. As a result, since the gas seal between the conductive oxidizer separator board 2 and the conductive fuel separator board 3, and the membrane electrode zygote 1 was made to form, the assembly process of the cell was able to be simplified.

[0027]

Demolition with a membrane electrode zygote and a separator board was easily completed by exposing the cell after test termination to the temperature more than the flow starting point of the thermoplastics used for the level difference dissolution member.

Since the membrane electrode zygote was separated easily [ an electrode substrate and an electrolyte membrane ] similarly, expense required for platinum recovery was able to be reduced.

[0028]

Embodiment 2.

Drawing 6 is a sectional view of the fuel cell concerning this embodiment of the invention 2. The fuel cell of this Embodiment 2 differs only in the fuel cell and level difference dissolution member of Embodiment 1, and since others are the same, explanation of the same portion is omitted. The thermoplastics of the polyolefin system of Embodiment 1 is impregnated with the nonwoven fabric of the super-thin textiles of polytetrafluoroethylene resin as a porous body of open pore, and the level difference dissolution members 23 and 24 are formed in it. It fills up with the hole of this nonwoven fabric with resin. The nonwoven fabric of the super-thin textiles of this polytetrafluoroethylene resin is [ thickness ] 7 micrometers in voidage at 70%.

[0029]

Next, the manufacturing method of the cell of the fuel cell of Embodiment 2 is explained with reference to drawing 7. Having added the nonwoven fabric of the super-thin textiles of polytetrafluoroethylene resin as a member of a cell differs from the manufacturing method of Embodiment 1, and others are the same.

First, the resin layer thickness adjustment films 25 and 26 are started to the shape of with the outer size of 10 cm x 20 cm, and an inside dimension of 7 cm x 14 cm RO from the nonwoven fabric of the super-thin textiles of polytetrafluoroethylene resin of 7 micrometers of thickness. Other members are prepared like Embodiment 1.

[0030]

Next, the member of a fuel cell is set to the plate 18 of the hotpress machine 19 like drawing 7. That is, the resin film 16 is set on the plate 18, It puts in order of the oxidant electrode substrate 9 and the resin film 15 so that the fuel electrode substrate 10, the resin layer thickness adjustment film 26, the electrolyte membrane 4, the resin layer thickness adjustment film 25, and the positive electrode catalyst layer 5 may become downward, as the negative-electrode catalyst bed 6 is suitable up on it.

Next, these are put at the pressure of about 1 kg/cm<sup>2</sup>, and the temperature of 150 \*\* with the

plates 17 and 18, and it is made a vacua after that, and bolting pressure is increased to  $5 \text{ kg/cm}^2$  and held for 3 minutes. The resin films 15 and 16 flow at this time, and the hole of the oxidant electrode substrate 9 and the fuel electrode substrate 10 is impregnated with that resin. Furthermore, the thermoplastics of the resin films 15 and 16 flows into the resin layer thickness adjustment film 25 and the resin layer thickness adjustment film 26. Next, bolting pressure was increased to  $10 \text{ kg/cm}^2$ , and was held for 2 minutes. Since the 14 positive electrode catalyst layers 5 and the negative-electrode catalyst bed 6 sank into the oxidant electrode substrate 9 and the fuel electrode substrate 10 selectively, respectively and became a thickness of 7 micrometers at this time, temperature was dropped to the room temperature. Thereby, the hole of the hole of the outer edge sections 11 and 12 of the oxidant electrode substrate 9 and the fuel electrode substrate 10, the resin layer thickness adjustment film 25, and the resin layer thickness adjustment film 26 is also fulfilled by thermoplastics. And the resin layer thickness adjustment films 25 and 26 are filled with resin, and serve as the level difference dissolution members 23 and 24. Excessive resin was disturbing from the heel of the oxidant electrode substrate 9 and the fuel electrode substrate 10. Thus, the cell of the fuel cell shown in drawing 6 was able to be formed.

[0031]

According to Embodiment 1, although the average thickness of the level difference dissolution members 7 and 8 was 7 micrometers, when the display flatness of an electrode substrate was bad, the level difference dissolution members 7 and 8 became thin selectively, and were thick conversely. However, in this Embodiment 2, since the thickness of the level difference dissolution members 23 and 24 was prescribed by the thickness of the nonwoven fabric of polytetrafluoroethylene resin, it was able to have thickness distribution with the more uniform level difference dissolution members 23 and 24. By furthermore making bolting pressure high, since it was prescribed by the thickness of the nonwoven fabric of polytetrafluoroethylene resin also when an electrode substrate had some thickness nonuniformity, it became possible to control the thickness of a catalyst bed.

[0032]

Since such a fuel cell can obtain the level difference dissolution member of uniform thickness, it can support an electrolyte membrane to homogeneity more.

[0033]

Embodiment 3.

Drawing 8 is a top view of the conductive fuel separator board of the fuel cell concerning this embodiment of the invention 3. Drawing 9 is a sectional view of the outer edge section of the cell which used the conductive fuel separator board of drawing 8.

The fuel gas flow route 14 is formed in a center section, and the conductive fuel separator board 3 is drilled so that the fuel supply port 27 which is open for free passage to one side of the end 31, and the fuel outlet 28 which is open for free passage at other ends 31 may penetrate the conductive fuel separator board 3. The oxidizer feed hopper 29 and the oxidizer outlet 30 are formed in the outer edge section. Although not illustrated, the oxidant gas passage 13 is established in a center section also like the conductive oxidizer separator board 2, and it is punctured so that the oxidizer feed hopper 29 which is open for free passage to one side of the end, and the oxidizer outlet 30 which is open for free passage at other ends may penetrate the conductive oxidizer separator board 2.

This conductive oxidizer separator board 2 and the conductive fuel separator board 3 are inserted from the both sides of the membrane electrode zygote 1 obtained by Embodiment 1, a hotpress is given, and a cell is produced.

[0034]

The end 31 of the fuel gas flow route 14 which was open for free passage to the fuel supply port 27 when produced in this way consists of space surrounded in the slot 32 established in the conductive fuel separator board 3 as shown in drawing 9, and the outer edge section 12 of the fuel electrode substrate 10 with which it filled up with thermoplastics. At this time, between the ridge 33 of the end 31 and the fuel electrode substrate 10 was being firmly fixed by the glue line

34 which consists of thermoplastics, and the gas leak was able to be prevented, without maintaining and changing rigidity firmly, also when differential pressure starts between the fuel gas flow route 14 and the oxidant gas passage 13.

[Brief Description of the Drawings]

[0035]

[Drawing 1] It is a sectional view of the fuel cell concerning this embodiment of the invention 1.

[Drawing 2] It is a figure showing signs that the membrane electrode zygote of the fuel cell of Embodiment 1 is laminated with a hotpress machine.

[Drawing 3] It is a sectional view of the fuel cell of a comparative example.

[Drawing 4] It is a figure showing change of the characteristic when operation evaluation of the fuel cell of Embodiment 1 and a comparative example is carried out.

[Drawing 5] It is a result when five fuel cells of Embodiment 1 and a comparative example are evaluated, respectively.

[Drawing 6] It is a sectional view of the fuel cell concerning this embodiment of the invention 2.

[Drawing 7] It is a figure showing signs that the membrane electrode zygote of the fuel cell of Embodiment 2 is laminated with a hotpress machine.

[Drawing 8] It is a top view of the conductive fuel separator board of the fuel cell concerning this embodiment of the invention 3.

[Drawing 9] It is a sectional view of the outer edge section of the cell using the conductive fuel separator board of Embodiment 3.

[Description of Notations]

[0036]

1 A membrane electrode zygote and 2 A conductive oxidizer separator board and 3 Conductive fuel separator board, 4 An electrolyte membrane and 5 A negative-electrode catalyst bed, and 7, 8, 23 and 24 A positive electrode catalyst layer and 6 Level difference dissolution member, 9 and 20 An oxidant electrode substrate, and 10 and 21 A fuel electrode substrate, and 11 and 12 Outer edge section, 13 An oxidant gas passage, 14 fuel gas flow routes, 15, 16 resin films, 17 and 18 [ A resin layer thickness adjustment film and 27 / A fuel supply port and 28 / A fuel outlet and 29 / An oxidizer feed hopper and 30 / An oxidizer outlet and 31 / An end and 32 / A slot and 33 / A ridge and 34 / Glue line. ] A gasket, and 25 and 26 A plate and 19 A hotpress machine and 22

[Translation done.]

**\* NOTICES \***

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- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

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**DESCRIPTION OF DRAWINGS**

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[Brief Description of the Drawings]

[0035]

[Drawing 1]It is a sectional view of the fuel cell concerning this embodiment of the invention 1.

[Drawing 2]It is a figure showing signs that the membrane electrode zygote of the fuel cell of Embodiment 1 is laminated with a hotpress machine.

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[Drawing 4]It is a figure showing change of the characteristic when operation evaluation of the fuel cell of Embodiment 1 and a comparative example is carried out.

[Drawing 5]It is a result when five fuel cells of Embodiment 1 and a comparative example are evaluated, respectively.

[Drawing 6]It is a sectional view of the fuel cell concerning this embodiment of the invention 2.

[Drawing 7]It is a figure showing signs that the membrane electrode zygote of the fuel cell of Embodiment 2 is laminated with a hotpress machine.

[Drawing 8]It is a top view of the conductive fuel separator board of the fuel cell concerning this embodiment of the invention 3.

[Drawing 9]It is a sectional view of the outer edge section of the cell using the conductive fuel separator board of Embodiment 3.

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[Translation done.]

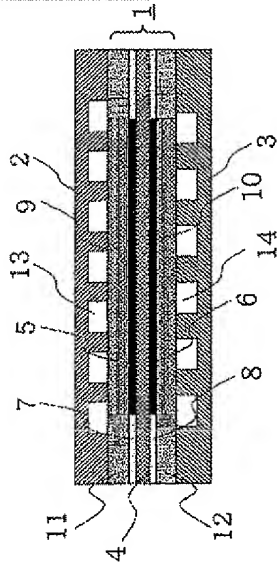
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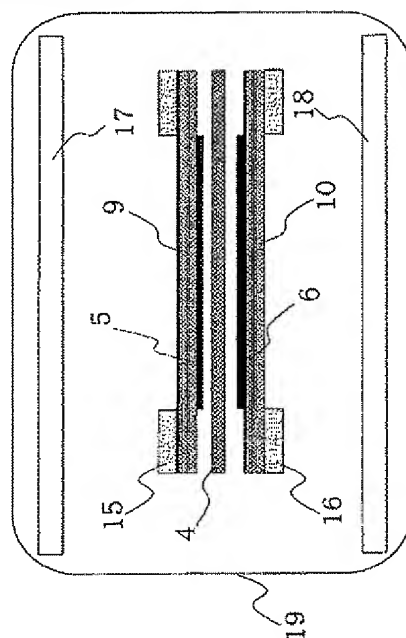
- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
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- 3.In the drawings, any words are not translated.

## DRAWINGS

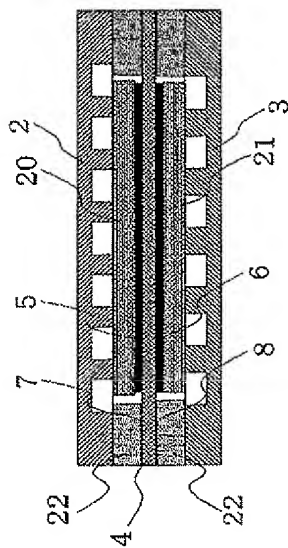
[Drawing 1]



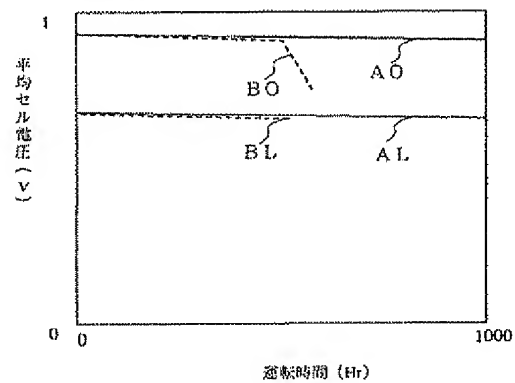
[Drawing 2]



[Drawing 3]



[Drawing 4]

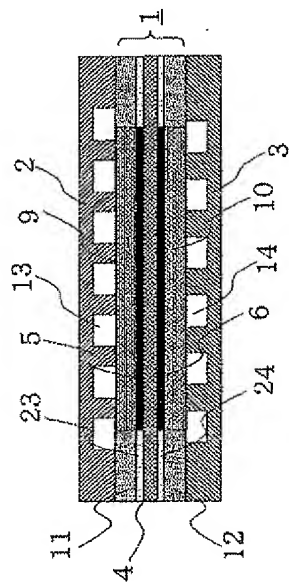


[Drawing 5]

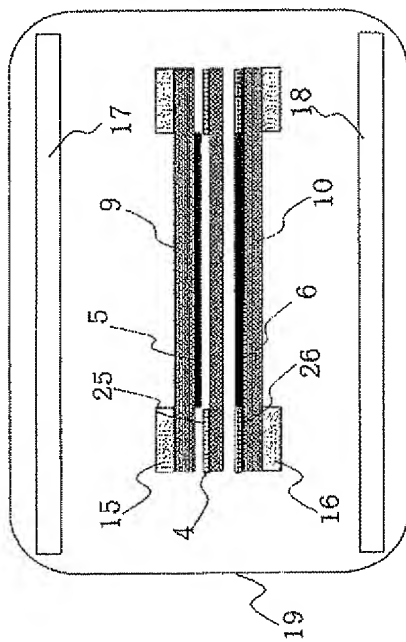
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セル温度		80°C	80°C	80°C	75°C	80°C
加湿温度		65°C	75°C	70°C	65°C	65°C
本発明	特性低下率*	10mV	5mV	7mV	5mV	12mV
従来	特性低下率*	13mV**	6mV	8mV**	7mV**	19mV**
	特性低下時間	620時間	—	750時間	700時間	540時間

[Drawing 6]

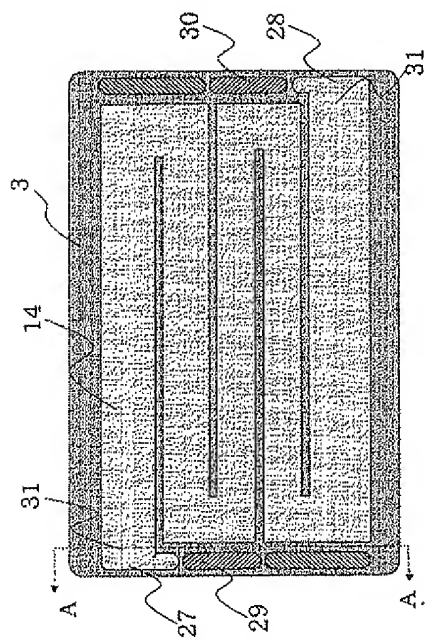




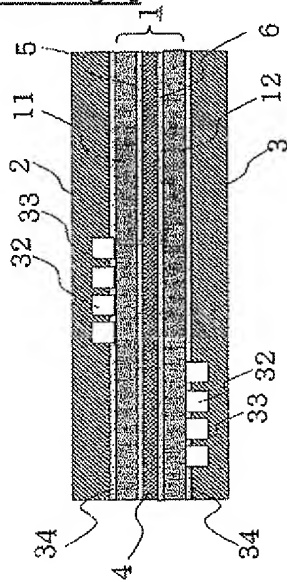
[Drawing 7]



[Drawing 8]



[Drawing 9]



[Translation done.]

JP 2005-135639 A

This document discloses a method of separating an electrode assembly from a pair of separators in a fuel cell in which a pair of separators sandwiches an electrode assembly and are bonded via a bonding portion. The document teaches that the separation can be performed easily by exposing the fuel cell in a temperature range that is not less than the flow starting temperature of the thermoplastic resin used as the bonding portion (Paragraph [0027]).

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(12) 公開特許公報(A)

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H01M 8/02

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テーマコード(参考)

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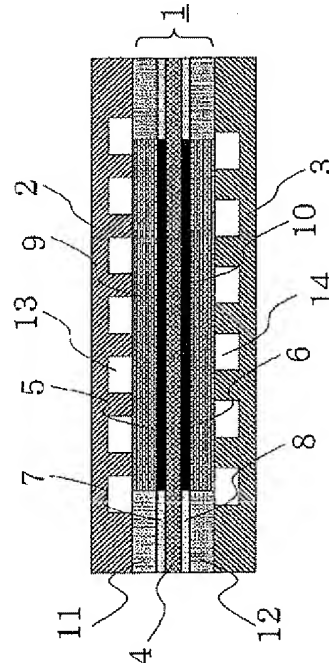
(54) 【発明の名称】 燃料電池およびその製造方法

## (57) 【要約】

【課題】 均一な圧力のもと電極基材により支持され、乾燥および湿潤の繰り返しによるストレスが加わっても膜破損の恐れのない固体高分子電解質膜を有する燃料電池とその製造方法を提供することである。

【解決手段】 燃料電池では、固体高分子電解質膜の中央部を両面から挟持した負極触媒層および正極触媒層を上記固体高分子電解質膜と同じ外形の燃料電極基材および酸化剤電極基材で外側から挟持してなる膜電極接合体を有する燃料電池であって、上記固体高分子電解質膜のうち上記負極触媒層および上記正極触媒層を囲繞する外縁部と上記燃料電極基材および酸化剤電極基材との隙間に段差解消部材を設けた。

【選択図】 図1



## 【特許請求の範囲】

## 【請求項 1】

固体高分子電解質膜の中央部に両面から接合された負極触媒層および正極触媒層を上記負極触媒層より大きな面積の燃料電極基材および上記正極触媒層より大きな面積の酸化剤電極基材でさらに両側から挟持してなる膜電極接合体を有する燃料電池において、

上記固体高分子電解質膜のうち上記負極触媒層および上記正極触媒層を囲繞する外縁部と上記燃料電極基材および上記酸化剤電極基材との隙間にそれぞれ段差解消部材が設けられたことを特徴とする燃料電池。

## 【請求項 2】

上記段差解消部材が熱可塑性樹脂からなることを特徴とする請求項 1 に記載の燃料電池

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## 【請求項 3】

上記段差解消部材が熱可塑性樹脂が充填された多孔質体からなることを特徴とする請求項 1 に記載の燃料電池。

## 【請求項 4】

負極触媒層および正極触媒層が固体高分子電解質膜に接するように上記負極触媒層が中央部に設けられた燃料電極基材と上記正極触媒層が中央部に設けられた酸化剤電極基材とを上記固体高分子電解質膜の両面に積層し、

さらに、上記燃料電極基材の上記固体高分子電解質膜に対面していない面に上記負極触媒層を囲繞するように棒状の熱可塑性樹脂シートを積層し、

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一方、上記酸化剤電極基材の上記固体高分子電解質膜に対面していない面に上記正極触媒層を囲繞するように棒状の熱可塑性樹脂シートを積層して積層体を形成し、

上記積層体の両側から加圧加熱して膜電極接合体を製造する工程を有することを特徴とする燃料電池の製造方法。

## 【発明の詳細な説明】

## 【技術分野】

## 【0001】

この発明は電気化学的な反応を利用して発電する燃料電池およびその製造方法に関する

## 【背景技術】

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## 【0002】

燃料電池は、電解質膜を介在して 1 対の電極を対向させ、この一方の電極に燃料を、他方の電極に酸化剤を供給し、燃料と酸化剤とを燃料電池内で電気化学的に反応させることにより化学エネルギーを直接電気エネルギーに変換する装置である。この燃料電池のうち固体高分子型燃料電池は電解質膜としてプロトン伝導性を有する固体高分子電解質膜を用いているので、高出力の特性が得られる。

この固体高分子型燃料電池は反応ガスを供給し続けることにより電気化学反応が継続する。このときに電気化学反応で重要な役割を果たす電解質膜のイオン伝導性は、固体高分子電解質膜の水分含有量にほぼ比例する。さらに、固体高分子電解質膜の水分含有量が反応ガスの湿度に依存しているので、反応ガスを加湿して運転する。

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## 【0003】

しかし、固体高分子電解質膜は乾燥すると縮み吸湿すると膨潤するので、運転と停止の繰り返しにより固体高分子電解質膜にストレスがかかる。さらに、酸化剤供給口に乾燥した空気を供給したとき、空気流路の上流域では固体高分子電解質膜が乾燥し、その下流域では生成水により固体高分子電解質膜が湿潤する。このようにして固体高分子電解質膜にストレスが加わるので、確実に固体高分子電解質膜を支えておかなければ固体高分子電解質膜が破損してしまうおそれがあった。

そこで、従来の燃料電池では、固体高分子電解質膜に処理を施して固体高分子電解質膜を確実に支持できるようにしている。例えば、固体高分子電解質膜が 1 対の電極より面積が大きいかつ 1 対の電極と接する通電部と 1 対の電極と接していない非通電部とを有して

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いる。その通電部と非通電部との境界部に補強材が含まれている。この補強材の材質としては含フッ素重合体を用いられている（例えば、特許文献1参照。）。

しかし、固体高分子電解質膜の通電部と補強材で補強された非通電部との境界部にストレスが集中し、境界部に沿って亀裂が生じるおそれがあった。

そこで、固体高分子電解質膜を支持する電極基材を補強して固体高分子電解質膜を確実に支持できるようにしている。例えば、電極基材が固体高分子電解質膜と同一の面積であり、かつ電極基材の周縁部が接着剤からなる緻密化剤で緻密化されている。この緻密化された周縁部で固体高分子電解質膜を支持し、かつガスシールしている。緻密化剤としてはポリテトラフルオロエチレン系のディスパージョンを使用し、周縁部に含浸後溶媒を取り除いて緻密化を行っている（例えば、特許文献2参照。）。

また、他の電極基材の補強方法としては、電極の発電領域を包囲する封止領域に射出成形可能な熱硬化性液体化合物を含浸し、硬化している（例えば、特許文献3参照。）。

【0004】

【特許文献1】特開2000-260443号公報

【特許文献2】特開平8-148170号公報

【特許文献3】特表2001-510932号公報

【発明の開示】

【発明が解決しようとする課題】

【0005】

しかし、上述の電極基材の補強方法では、電極基材に形成された触媒層の厚みの分、周縁部と発電部とで触媒層を含んだ電極基材の厚みが異なる。このため外部から電極基材を介して固体高分子電解質膜に加わる圧力が、固体高分子電解質膜の周縁部と発電部とでは異なり、周縁部での支持が弱くなってしまうという問題があった。

【0006】

この発明の目的は、均一な圧力のもと電極基材により支持され、乾燥および湿潤の繰り返しによるストレスが加わっても膜破損のおそれのない固体高分子電解質膜を有する燃料電池とその製造方法を提供することである。

【課題を解決するための手段】

【0007】

この発明にかかる燃料電池では、固体高分子電解質膜の中央部に両面から接合された負極触媒層および正極触媒層を上記負極触媒層より大きな面積の燃料電極基材および上記正極触媒層より大きな面積の酸化剤電極基材でさらに両側から挟持してなる膜電極接合体を有する燃料電池において、上記固体高分子電解質膜のうち上記負極触媒層および上記正極触媒層を囲繞する外縁部と上記燃料電極基材および上記酸化剤電極基材との隙間にそれぞれ段差解消部材が設けられた。

【発明の効果】

【0008】

この発明の燃料電池に係わる効果は、段差解消部材により触媒層に係わる発電部と外縁部との間に見られる段差を解消し、電解質膜を触媒層と段差解消部材で平坦に支持するので、電解質膜に加わるストレスを均一にすることができる。その結果、電解質膜の破損を防止することができる。

【発明を実施するための最良の形態】

【0009】

実施の形態1.

図1はこの発明の実施の形態1に係わる固体高分子型燃料電池の断面図である。

この固体高分子型燃料電池（以下、燃料電池と称す。）の単電池は、膜電極接合体1とその膜電極接合体1を両側から挟持する導電性酸化剤セパレータ板2および導電性燃料セパレータ板3とを有する。

この膜電極接合体1は、プロトン伝導性の固体高分子電解質膜（以下、電解質膜と称す。）4、電解質膜4の片面の中央部に接する正極触媒層5、電解質膜4の他の片面の中央

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部に接する負極触媒層 6、正極触媒層 5 と負極触媒層 6 のそれぞれの外周に接し、電解質膜 4 の外縁部に面した段差解消部材 7、8、正極触媒層 5 と段差解消部材 7 とを覆う酸化剤電極基材 9、負極触媒層 6 と段差解消部材 8 とを覆う燃料電極基材 10 を有する。酸化剤電極基材 9 と燃料電極基材 10 の段差解消部材 7、8 がそれぞれ面する外縁部 11、12 には熱可塑性樹脂が充填されている。

#### 【0010】

また、導電性酸化剤セパレータ板 2 は、酸化剤電極基材 9 に面する面に酸化剤を流す酸化剤ガス流路 13 が設けられている。さらに、導電性燃料セパレータ板 3 は、燃料電極基材 10 に面する面に燃料を流す燃料ガス流路 14 が設けられている。この酸化剤ガス流路 13 は、導電性酸化剤セパレータ板 2 の外縁部に延在し、さらにその導電性酸化剤セパレータ板 2 の外縁部に厚み方向に穿設された穴に連なっている。単電池を複数個積層するときこの穴は上下に積層されている単電池の導電性燃料セパレータ板 3 に設けられた穴と連なり、さらにその上の導電性酸化剤セパレータ板 2 に設けられた穴と連なっていく。一番上に積層された単電池の導電性酸化剤セパレータ板 2 に設けられた穴を酸化剤供給口としてそこに酸化剤が供給される。一方、一番下に積層された単電池の導電性燃料セパレータ板 3 に設けられた穴を酸化剤排出口としてそこから余った酸化剤が排出される。燃料に関しても同様にして供給・排出される。

#### 【0011】

電解質膜 4 は、外形が 10 cm × 20 cm で膜厚が 50 μm のパーフルオロスルホン酸膜であるナフィオン（登録商標）膜である。

正極触媒層 5 は、50 重量%白金が担持されたカーボンブラック粒子とパーフルオロ系高分子電解質との混合物が電解質膜 4 の中央部の片面に外形が 7 cm × 14 cm で膜厚が 14 μm で積層されている。正極触媒層 5 は、酸化剤電極基材 9 に 7 μm 押し込まれており、酸化剤電極基材 9 の表面と正極触媒層 5 の電解質膜 4 に面する面との段差は 7 μm になっている。

負極触媒層 6 は、50 重量%白金-ルテニウム系合金が担持されたカーボンブラック粒子とパーフルオロ系高分子電解質との混合物が電解質膜 4 の中央部の正極触媒層 5 が形成された面の反対面に外形が 7 cm × 14 cm で膜厚が 14 μm で積層されている。負極触媒層 6 は、燃料電極基材 10 に 7 μm 押し込まれており、燃料電極基材 10 の表面と負極触媒層 6 の電解質膜 4 に面する面との段差は 7 μm になっている。

段差解消部材 7、8 は、熱可塑性樹脂からなり、外寸が 10 cm × 20 cm、内寸が 7 cm × 14 cm、膜厚が 7 μm である。

#### 【0012】

酸化剤電極基材 9 と燃料電極基材 10 は、空隙率 80% のカーボンペーパーであり、外形が 10 cm × 20 cm で膜厚が 300 μm である。また、酸化剤電極基材 9 と燃料電極基材 10 のそれぞれの外縁部 11、12 の空孔には段差解消部材 7、8 と同一の熱可塑性樹脂が充填されている。

導電性酸化剤セパレータ板 2 と導電性燃料セパレータ板 3 は、黒鉛を樹脂によって結合した黒鉛板であり、それらの片面の中央部の 7 cm × 14 cm の領域にそれぞれ酸化剤ガス流路 13 と燃料ガス流路 14 が設けられている。

#### 【0013】

熱可塑性樹脂は、ポリオレフィン系樹脂が用いられている。なお、熱可塑性樹脂として、燃料電池が稼働しているときの最大温度以上にガラス転移温度があり、かつ電解質膜 4 の耐熱温度以下に軟化点温度を有する樹脂であればこの発明に適用することができる。例えば、ポリエチレン、ポリプロピレンに代表されるポリオレフィン系樹脂およびポリオレフィンとポリ酢酸ビニルなどの共重合樹脂がある。また、ナイロン 11、ナイロン 12 などに代表される共重合ナイロン系樹脂、ポリエチレンテレフタレートやその共重合体に代表されるポリエステル系樹脂が挙げられる。さらに、ポリブチレン樹脂、ポリメタクリル酸メチル系樹脂、無定型ポリアミド樹脂などを使用することができる。

#### 【0014】

次に、この燃料電池の製造方法を図2を参照して説明する。

まず、酸化剤電極基材9と燃料電極基材10とを、厚み300 $\mu$ m、空隙率80%のカーボンペーパー（東レ（株）製TGP-H-90）から10cm $\times$ 20cmに切り出す。また、膜厚300 $\mu$ mのポリオレフィン系の熱可塑性樹脂膜から外寸10cm $\times$ 20cm、内寸7cm $\times$ 14cmの口の字型に樹脂フィルム15、16を切り出す。この樹脂フィルム15、16の熱可塑性樹脂の流動開始温度は130 $^{\circ}$ Cである。流動開始温度は、高化式フローテスター（0.5mm $\phi$  $\times$ 1mm $\times$ 10kg/cm $^2$ ）を用いて、昇温速度3 $^{\circ}$ C/minで測定された。また、厚さ50 $\mu$ mのデュポン製ナフィオン膜から外形10cm $\times$ 20cmに電解質膜1を切り出す。

#### 【0015】

次に、正極触媒層5と負極触媒層6の形成について説明する。正極触媒としては白金をカーボンブラック上に50重量%担持したものをを用いている。この正極触媒1重量部に水1重量部とパーフルオロ系高分子電解質溶液（旭硝子（株）製フレミオン（登録商標）9%溶液）3重量部を添加し、攪拌混合して均一な正極触媒ペーストを作製する。また、負極触媒としては白金-ルテニウム系合金をカーボンブラック上に50重量%担持したものをを用いている。この負極触媒1重量部に水1重量部とパーフルオロ系高分子電解質溶液（旭硝子（株）製フレミオン（登録商標）9%溶液）6重量部を添加し、攪拌混合して均一な負極触媒ペーストを作製する。次に、この正極触媒ペーストを酸化剤電極基材9の中央部に外形7cm $\times$ 14cmになるようにスクリーン印刷し、減圧乾燥して、乾燥後膜厚14 $\mu$ mになるように正極触媒層5を形成した。さらに、負極触媒ペーストを燃料電極基材10の中央部に外形7cm $\times$ 14cmになるようにスクリーン印刷し、減圧乾燥して、乾燥後膜厚14 $\mu$ mになるように負極触媒層6を形成した。

#### 【0016】

次に、ホットプレス機19の平板18に図2のように燃料電池の部材をセットする。つまり、樹脂フィルム16を平板18上にセットし、その上に負極触媒層6が上方に向くようにして燃料電極基材10、電解質膜4、正極触媒層5が下向きになるように酸化剤電極基材9、樹脂フィルム15の順に積み重ねる。

次に、平板17、18でこれらを圧力1kg/cm $^2$ 程度、温度150 $^{\circ}$ Cで挟み込み、その後真空状態にして締付け圧を5kg/cm $^2$ に上げて3分間保持する。このとき樹脂フィルム15、16が流動して酸化剤電極基材9と燃料電極基材10との空孔にその樹脂が含浸していく。さらに、電解質膜4と酸化剤電極基材9との隙間および電解質膜4と燃料電極基材10との隙間に樹脂フィルム15、16の熱可塑性樹脂が流れ込む。次に、締付け圧を10kg/cm $^2$ に上げて2分間保持した。このとき、14 $\mu$ mあった正極触媒層5と負極触媒層6とがそれぞれ酸化剤電極基材9と燃料電極基材10とに部分的にめり込み7 $\mu$ mの厚みになるので、温度を室温まで降下させた。熱可塑性樹脂によって酸化剤電極基材9と燃料電極基材10の外縁部11、12の空孔が満たされるとともに、酸化剤電極基材9および燃料電極基材10と電解質膜4との隙間が埋められて、段差解消部材7、8が形成される。正極触媒層5および負極触媒層6の接した酸化剤電極基材9および燃料電極基材10の部分に0.5mm程度の幅で樹脂が流れ込んでいたが、電極の有効面積の損失は約2%と無視できる程度であった。余分な樹脂は酸化剤電極基材9および燃料電極基材10の外端部からはみだしていた。このようにして図1に示す燃料電池の単電池を形成することが出来た。

#### 【0017】

なお、この実施の形態1において樹脂フィルム15、16の中央の穴の内寸を正極触媒層5および負極触媒層6の外形と同一の形状としたが、中央の穴の内寸を1mm大きくすることにより電極有効面積の損失をほとんど無くすることができた。

#### 【0018】

次に、燃料電池の動作について説明する。導電性酸化剤セパレータ板2の図示しない酸化剤供給口より供給された酸化剤としての酸素は、酸化剤ガス流路13を通り、酸化剤電極基材9内を拡散して正極触媒層5に供給される。一方、燃料としての水素は空気と同様

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に、燃料ガス流路14を通り、燃料電極基材10内を拡散して負極触媒層6に供給される。このとき、正極触媒層5と負極触媒層6とは電氣的に外部で接続されているので、正極触媒層5では式(1)の反応が生じ、酸化剤ガス流路13を通して未反応酸素と水とが図示しない酸化剤排出口から排出される。また、このとき負極触媒層6では式(2)の反応が生じ未反応水素は同様に燃料ガス流路14を通じて図示しない燃料排出口より排出される。



このとき負極触媒層6上で水素はイオン化されてプロトンとなり、水を伴って電解質膜4中を正極触媒層5上まで移動し、酸素と反応して水を生ずる。

#### 【0019】

次に、この発明の実施の形態1の燃料電池と比較試験を行うために図3に示す比較例の燃料電池を作製した。この比較例の燃料電池が実施の形態1の燃料電池と異なっているところは、酸化剤電極基材20、燃料電極基材21とガasket22である。その他は同様であるので、同様な部分の説明を省略する。

図3において酸化剤電極基材20と燃料電極基材21の材質と厚みは実施の形態1と同様である。酸化剤電極基材20と燃料電極基材21の外形寸法が正極触媒層5と負極触媒層6の外形寸法と同一である。また、正極触媒層5と負極触媒層6もあらかじめホットプレスを施して酸化剤電極基材20と燃料電極基材21に7μmだけ埋め込んである。ガasket22は、ポリオレフィン系樹脂板から外形10cm×20cm、内寸8cm×15cmの口の字状に打ち抜いて用意した。これらを図3のように積層して比較例の燃料電池の単電池を作製した。

#### 【0020】

この燃料電池の単電池を4つ用いてショートスタックを試作し、運転評価を実施した。比較例の燃料電池も単電池を4つ用いて並行して運転評価を実施し、対比を行った。

これらのショートスタックの温度を80℃に保った状態で、露点65℃の空気を利用率50%相当流量流し、25Aの電流で発電運転を実施した。このとき燃料として一酸化炭素を20ppm含有する改質模擬ガス(水素75%、残り二酸化炭素)を燃料利用率80%で供給した。この時酸化剤供給口の相対湿度は53%となる。一方酸化剤排出口では燃料電池反応により水が生成するため、空気中の水分量が増大し、相対湿度が80%に達した。従って、空気の上流に相当する領域では、電解質膜4が乾燥してイオン抵抗が増大する。一方下流域では、生成水により電解質膜4の水分含有量が増加してイオン抵抗が減少する。この時、初期の燃料電池の単電池の電圧が750mVとなり、開回路電圧も960mVとなっていた。そして8時間運転し、8時間停止(負荷・ガス停止、温度室温)するというサイクルを繰り返した。図4に運転時間毎の単電池の電圧と開回路電圧を示す。図4中のALが実施の形態1の燃料電池の25A負荷時の平均単電池電圧、AOが開回路電圧である。一方、BL、BOが比較例の燃料電池の25A負荷時の平均単電池電圧と開回路電圧である。

#### 【0021】

実施の形態1の燃料電池では運転時間の経過とともに特性の低下は見られるものの、1000時間経っても25A負荷時の単電池電圧は740mVと試験初期の単電池電圧から10mVだけ低下するに留まり、開回路電圧も955mVと試験初期の値より数mVしか低下しなかった。一方、比較例の燃料電池では600時間までは実施の形態1の燃料電池と同様の特性を示していたが、それ以降に突然1部の開回路電圧が700mV以下に低下した。単電池の温度の制御ができなくなったので運転を中止して分解すると、開回路電圧の低下した単電池のガasket22と電極基材の隙間部分の電解質膜4が破れていた。また、他の単電池も電解質膜4が破れはしなかったがガasket22と電極基材20、21との隙間部分の電解質膜4にしわが発生しており、もろくなっていた。この試験を運転温度と湿度の組合せを変えて5回試みた。図5にその試験結果の概要を示す。実施の形態1の燃料電池では特性低下量に差はあったものの安定した特性を示して試験が継続できた。

一方、比較例の燃料電池では、加湿温度が高いケース2では実施の形態1の燃料電池と同様な特性の安定性を示していたが、加湿温度が低い条件においては、数百時間で開回路電圧が低下し、電解質膜4が破損した。

#### 【0022】

この実施の形態1の燃料電池では、外縁部の電解質膜が電氣的に絶縁されているため、電解質膜4が外気と触れていても、内部の燃料流路からのイオン伝導経路が極端に長くなって、実質的に局所電池を形成することがなく、腐食や燃料損失の心配がなくなった。

#### 【0023】

このような燃料電池は、段差解消部材7、8により触媒層5、6に係わる発電部と外縁部との間に見られる段差を解消し、電解質膜4を触媒層5、6と段差解消部材7、8とで平坦に支持するので、電解質膜4に加わるストレスを均一にすることができる。その結果、電解質膜の破損を防止することができる。

#### 【0024】

また、このような燃料電池の製造方法は、ホットプレス時に熱可塑性樹脂が電解質膜4と電極基材9、10との隙間に流れ込むので、燃料電池に使用される部材の寸法のばらつきなどを吸収して触媒層5、6と段差解消部材7、8との電解質膜4に接する面を平坦にすることができる。

#### 【0025】

また、熱可塑性樹脂を用いると段差解消部材7、8を構成する樹脂と電極基材9、10の空孔に含浸された樹脂とが連続した樹脂膜となりガスシール性が向上する。

#### 【0026】

なお、段差解消部材に用いた熱可塑性樹脂を流動開始点が110℃（融点92℃）のもので膜電極接合体1を作製し、その膜電極接合体1と導電性酸化剤セパレータ板2および導電性燃料セパレータ板3とを順次積層して単電池を形成した後に110℃で加熱した。その結果、導電性酸化剤セパレータ板2および導電性燃料セパレータ板3と膜電極接合体1との間のガスシールを形成させることができるので、単電池の組立工程を簡略化することができた。

#### 【0027】

また、試験終了後の単電池を段差解消部材に用いた熱可塑性樹脂の流動開始点以上の温度にさらすことによって、膜電極接合体とセパレータ板との解体が容易にできた。

また、膜電極接合体も同様にして電極基材と電解質膜とに簡単に分離することができるので、白金回収に必要な費用を削減することができた。

#### 【0028】

実施の形態2.

図6はこの発明の実施の形態2に係わる燃料電池の断面図である。この実施の形態2の燃料電池は実施の形態1の燃料電池と段差解消部材だけが異なっており、その他は同様であるので、同様な部分の説明を省略する。段差解消部材23、24は、オープンポアの多孔質体としてのポリテトラフルオロエチレン樹脂の極細繊維の不織布に実施の形態1のポリオレフィン系の熱可塑性樹脂が含浸されて形成されている。この不織布の空孔が樹脂によって充填されている。このポリテトラフルオロエチレン樹脂の極細繊維の不織布は空隙率が70%で膜厚が7μmである。

#### 【0029】

次に、実施の形態2の燃料電池の単電池の製造方法について図7を参照して説明する。なお、実施の形態1の製造方法とは単電池の部材としてポリテトラフルオロエチレン樹脂の極細繊維の不織布を追加していることが異なりその他は同様である。

まず、膜厚7μmのポリテトラフルオロエチレン樹脂の極細繊維の不織布から、外寸10cm×20cm、内寸7cm×14cmの口の字型に樹脂膜厚調整フィルム25、26を切り出す。その他の部材は実施の形態1と同様にして準備する。

#### 【0030】

次に、ホットプレス機19の平板18に図7のように燃料電池の部材をセットする。つ

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まり、樹脂フィルム16を平板18上にセットし、その上に負極触媒層6が上方に向くようにして燃料電極基材10、樹脂膜厚調整フィルム26、電解質膜4、樹脂膜厚調整フィルム25、正極触媒層5が下向きになるように酸化剤電極基材9、樹脂フィルム15の順に積み重ねる。

次に、平板17、18でこれらを圧力1kg/cm<sup>2</sup>程度、温度150℃で挟み込み、その後真空状態にして締付け圧を5kg/cm<sup>2</sup>に上げて3分間保持する。このとき樹脂フィルム15、16が流動して酸化剤電極基材9と燃料電極基材10の空孔にその樹脂が含浸していく。さらに樹脂膜厚調整フィルム25と樹脂膜厚調整フィルム26に樹脂フィルム15、16の熱可塑性樹脂が流れ込む。次に、締付け圧を10kg/cm<sup>2</sup>に上げて2分間保持した。このとき、14μmあった正極触媒層5と負極触媒層6とがそれぞれ酸化剤電極基材9と燃料電極基材10とに部分的にめり込み7μmの厚みになるので、温度を室温まで降下させた。これにより、熱可塑性樹脂によって酸化剤電極基材9と燃料電極基材10の外縁部11、12の空孔と樹脂膜厚調整フィルム25および樹脂膜厚調整フィルム26の空孔も満たされる。そして、樹脂膜厚調整フィルム25、26が樹脂で満たされ、段差解消部材23、24となる。余分な樹脂は酸化剤電極基材9および燃料電極基材10の外端部からはみだしていた。このようにして図6に示す燃料電池の単電池を形成することが出来た。

#### 【0031】

実施の形態1では、段差解消部材7、8の平均厚みは7μmであったが、電極基材の平坦度が悪いときに段差解消部材7、8が部分的に薄くなったり逆に厚くなったりしていた。しかし、この実施の形態2ではポリテトラフルオロエチレン樹脂の不織布の厚みにより段差解消部材23、24の厚みが規定されるため、段差解消部材23、24がより均一な厚み分布をもつことができた。さらに締付け圧を高くすることにより、電極基材に多少の厚みムラがあった場合にもポリテトラフルオロエチレン樹脂の不織布の厚みで規定されるので触媒層の厚みを制御することが可能となった。

#### 【0032】

このような燃料電池は、均一な厚みの段差解消部材を得ることができるので、電解質膜をより均一に支持できる。

#### 【0033】

実施の形態3.

図8はこの発明の実施の形態3に係わる燃料電池の導電性燃料セパレータ板の平面図である。図9は図8の導電性燃料セパレータ板を用いた単電池の外縁部の断面図である。

導電性燃料セパレータ板3は、燃料ガス流路14が中央部に設けられ、その端部31の一方に連通する燃料供給口27と他の端部31に連通する燃料排出口28とが導電性燃料セパレータ板3を貫通するように穿設されている。さらに、外縁部には酸化剤供給口29と酸化剤排出口30が設けられている。図示していないが、導電性酸化剤セパレータ板2にも同様に酸化剤ガス流路13が中央部に設けられ、その端部の一方に連通する酸化剤供給口29と他の端部に連通する酸化剤排出口30とが導電性酸化剤セパレータ板2を貫通するように穿設されている。

この導電性酸化剤セパレータ板2と導電性燃料セパレータ板3とを実施の形態1で得られた膜電極接合体1の両側から挟んでホットプレスを施して単電池を作製する。

#### 【0034】

このように作製すると燃料供給口27に連通した燃料ガス流路14の端部31は、図9に示すように導電性燃料セパレータ板3に設けられた溝32と熱可塑性樹脂が充填された燃料電極基材10の外縁部12とで囲まれた空間からなる。このとき、端部31の畝33と燃料電極基材10間が熱可塑性樹脂からなる接着層34により強固に固定されており、燃料ガス流路14と酸化剤ガス流路13間で差圧が掛かった場合にもしっかりと剛性を保ち、変型すること無くガスリークを防止することが出来た。

#### 【図面の簡単な説明】

#### 【0035】

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【図 1】この発明の実施の形態 1 に係わる燃料電池の断面図である。

【図 2】実施の形態 1 の燃料電池の膜電極接合体をホットプレス機で積層する様子を示す図である。

【図 3】比較例の燃料電池の断面図である。

【図 4】実施の形態 1 と比較例との燃料電池とを運転評価したときの特性の変化を示す図である。

【図 5】実施の形態 1 と比較例との燃料電池をそれぞれ 5 個評価したときの結果である。

【図 6】この発明の実施の形態 2 に係わる燃料電池の断面図である。

【図 7】実施の形態 2 の燃料電池の膜電極接合体をホットプレス機で積層する様子を示す図である。

【図 8】この発明の実施の形態 3 に係わる燃料電池の導電性燃料セパレータ板の平面図である。

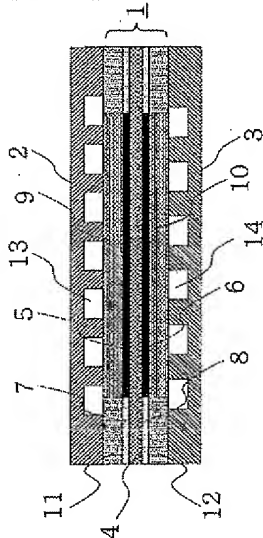
【図 9】実施の形態 3 の導電性燃料セパレータ板を用いた単電池の外縁部の断面図である。

【符号の説明】

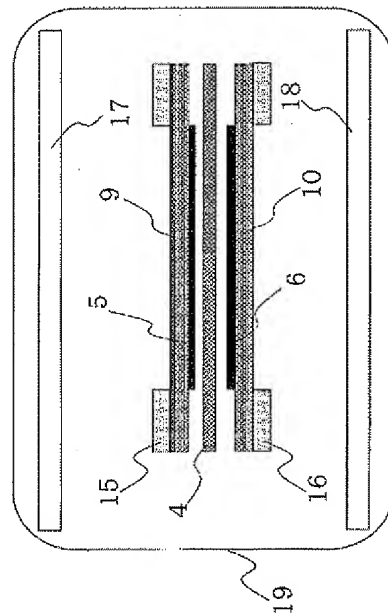
【0036】

1 膜電極接合体、2 導電性酸化剤セパレータ板、3 導電性燃料セパレータ板、4 電解質膜、5 正極触媒層、6 負極触媒層、7、8、23、24 段差解消部材、9、20 酸化剤電極基材、10、21 燃料電極基材、11、12 外縁部、13 酸化剤ガス流路、14 燃料ガス流路、15、16 樹脂フィルム、17、18 平板、19 ホットプレス機、22 ガasket、25、26 樹脂膜厚調整フィルム、27 燃料供給口、28 燃料排出口、29 酸化剤供給口、30 酸化剤排出口、31 端部、32 溝、33 畝、34 接着層。

【図 1】

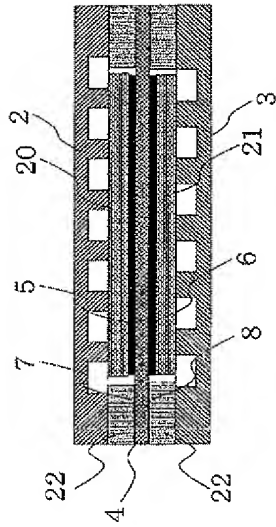


【図 2】

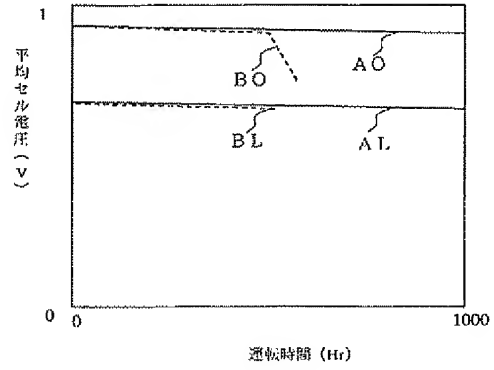




【図 3】



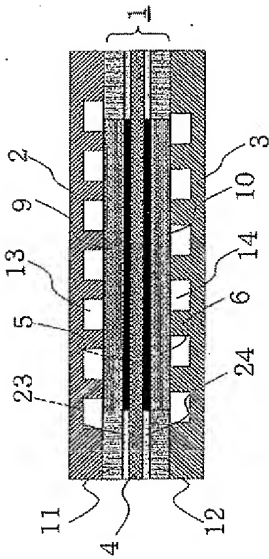
【図 4】



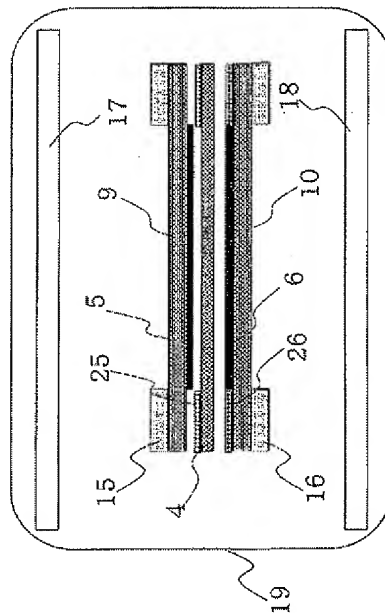
【図 5】

試験		1	2	3	4	5
セル温度		80℃	80℃	80℃	75℃	80℃
加温温度		65℃	75℃	70℃	65℃	65℃
本発明	特性低下率※	10mV	5mV	7mV	5mV	12mV
従来	特性低下率※	13mV**	6mV	8mV**	7mV**	10mV**
	開回路低下時間	620時間	—	750時間	700時間	540時間

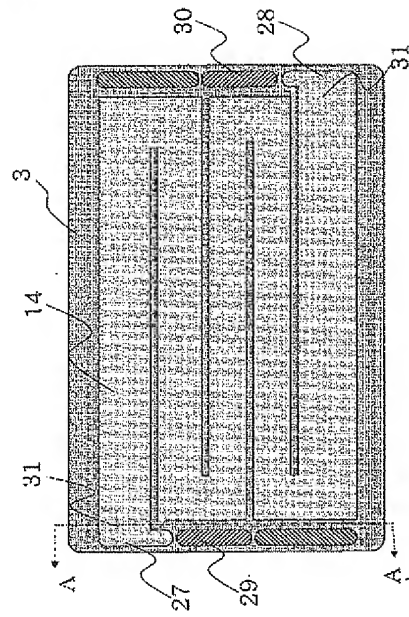
【図 6】



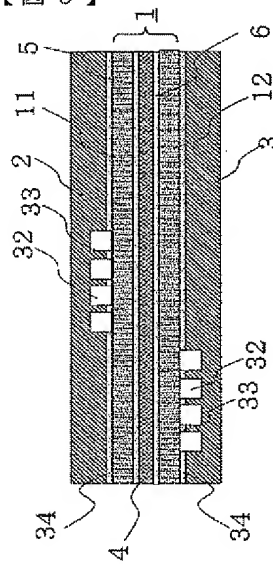
【図 7】



【図 8】



【図 9】



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フロントページの続き

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